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STRUCTURE OF THE $BaO - Al_2O_3 - SiO_2$ SYSTEM (A REVIEW)

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The results of theoretical calculations and experimental studies of the ternary system $BaO - Al_2O_3 - SiO_2$ in the subsolidus range at temperatures of 1200 – 1400°C are considered. Complete splitting of this system into elementary polytypes is performed, a topological graph of the relationship between these polytypes is shown, and geometrical characteristics of the binary and ternary compounds comprising this system are supplied.

In view of the progress in engineering, the requirements imposed on traditional silicate materials become increasingly strict, which makes it necessary to develop new materials with prescribed sets of properties. Such materials can be developed by researching physicochemical systems, the phases emerging in them, and their stable combinations. Such research is necessary for understanding and predicting processes occurring in materials of complex compositions at high temperatures and for solving practical problems, which include selection of compositions, development of rational methods for their treatment, control of properties of obtained products, etc. All this primarily concerns solid materials; consequently, the structure of systems is mainly considered in the subsolidus.

The ternary system $BaO - Al_2O_3 - SiO_2$ is undoubtedly interesting for the synthesis of new promising materials that combine such valuable and specific properties as high refractoriness, heat resistance, mechanical strength, chemical strength, protection from ionizing radiation, and good electrophysical parameters. Compositions of this system are used to obtain ceramics and glass celsian-based ceramics used in high-frequency engineering [1, 2]. Furthermore, some compounds of this system have clearly expressed binding properties, quickly cure, reach substantial mechanical strength, and can serve as a basis for developing highly effective special barium-containing cements [3].

The $BaO - Al_2O_3 - SiO_2$ system was studied in [4 – 7]; however, the results of these studies are contradictory and incomplete. It should be noted that data found in the reference literature do not represent a complete picture of the subsolidus structure of the system, since they do not take into account more recent data on the system structure and binary and ternary compounds emerging in this system. Consequently, additional research and clarification of the subsolidus structure of the $BaO - Al_2O_3 - SiO_2$ system is needed in order to fully represent this structure and to develop the physicochemical principles of production of silicate materials for various functional purposes.

To solve this problem, we used the method of splitting a multicomponent system into elementary polytypes (in the case of ternary system, into elementary triangles). The advisability of this method in studying multicomponent systems was proposed by Kurnakov in his classical studies on the topology of a chemical diagram [8]. Splitting a system into elementary polytypes makes it possible with a minimum number of experiments to represent the system structure as a whole, to identify individual particular systems, which, if needed, can be investigated in detail, to define the direction and type of reactions occurring in the system, stable groups of coexisting phases, etc.

The ternary system $BaO - Al_2O_3 - SiO_2$ consists of three particular systems: $BaO - SiO_2$, $BaO - Al_2O_3$, and $Al_2O_3 - SiO_2$.

Seven chemical compounds are formed in the $BaO - SiO_2$ system: $BaSi_2O_5$ congruently melting at a temperature of 1420°C [9]; $Ba_3Si_5O_{13}$ with incongruent melting at 1423°C [10]; $Ba_5Si_8O_{21}$ melting congruently at 1446°C [10], $Ba_2Si_3O_8$ with congruent melting at 1447°C [9]; $BaSiO_3$ with congruent melting at 1604°C; Ba_2SiO_4 melting congruently at 2050°C, and Ba_3SiO_5, which is stable only up to 1800°C and decomposes into barium orthosilicate and barium oxide above this temperature [9 – 13].

The following compounds are formed in the particular system $BaO - Al_2O_3$: $Ba_8Al_2O_{11}$ stable in an interval of 1050 – 1400°C [14] (according to other data, this compounds exists in the system already at 900°C [15]); $Ba_4Al_2O_7$ melting without decomposition at 1560°C [15], and barium aluminates of the compositions $Ba_3Al_2O_6$, $BaAl_2O_4$, and

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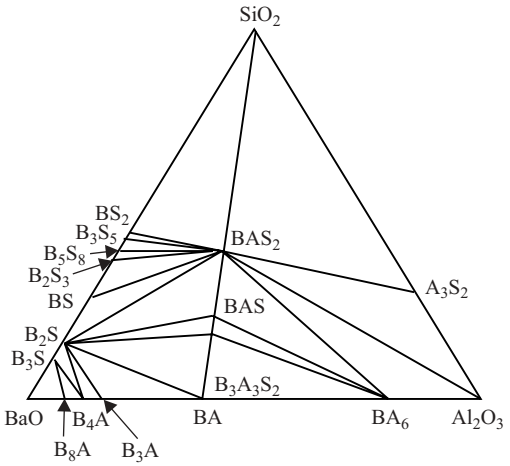

Fig. 1. Elementary triangles of $BaO - Al_2O_3 - SiO_2$ system: B) BaO, A) Al_2O_3, S) SiO_2.

$BaAl_{12}O_{19}$ with congruent melting at temperatures of 1750, 1830, and 1900°C, respectively [16]. Furthermore, highly basic barium aluminate of the compositions $Ba_5Al_2O_8$, $Ba_7Al_2O_{10}$ and $Ba_{10}Al_2O_{13}$, which are stable at temperature below 940, 1050, and 1130°C, respectively, are formed in the system [14].

In the $Al_2O_3 - SiO_2$ system there is only one chemical compound, namely, mullite $Al_6Si_2O_{13}$ melting without decomposition at a temperature of 1850°C [17].

There are data on three barium aluminosilicates in the literature. The main ternary compound in the $BaO - Al_2O_3 - SiO_2$ system is celsian $BaAl_2Si_2O_8$ melting congruently at a temperature of 1750 ± 10°C [4] and having a natural analog, namely, barium feldspar (paracelsian). Two compounds have been synthesized: $BaAl_2SiO_6$ [18] melting incongruently at a temperature of 1400°C [19] and according to the data in [20], above 1550°C, and $Ba_3Al_6Si_2O_{16}$ melting with decomposition at 1550°C [4, 21].

Evaluation of the protective properties of all ternary compounds in the system $BaO - Al_2O_3 - SiO_2$ was performed in [21] and manifestation of their binding properties in hydrothermal curing was theoretically substantiated and experimentally corroborated. It was established that the most effective service properties are found in the compound $Ba_3Al_6Si_2O_{16}$ combining high mechanical strength (102 MPa after hydrothermal treatment) and a high coefficient of mass absorption of γ-radiation (183.3 cm^2/g). This makes it possible to use as a component in protective binding materials applied in making products that serve under the conditions of hard radiation fields.

The authors of [21] considers the subsolidus structure of the $BaO - Al_2O_3 - SiO_2$ system in a temperature interval of 1200 – 1400°C, since the main phase-formation processes during a directed synthesis of materials of various destination occur precisely within this interval. Accordingly, this study took into account only those phases that are stable within the selected temperature interval. Altogether 19 phases were taken into account in studying the system structure: 3 oxides comprising the system, 13 binary phases, and 3 ternary compounds.

Since there are contradictory data in the literature on the subsolidus structure of a zone limited by the phases $BaSi_2O_5$, $BaAl_2Si_2O_8$, $Al_6Si_2O_{13}$, and SiO_2 (the authors of [4] maintain that sanbornite and mullite coexist in this zone, and data from [5 – 7] report the existence of celsian and silica), its is interesting to clarify its structure using the method of thermodynamic analysis.

The following reaction was subjected to thermodynamic analysis:

$$3BaAl_2Si_2O_8 + 2SiO_2 = 3BaSi_2O_5 + Al_6Si_2O_{13}.$$

The initial data for the calculation were taken from the literature [22]. The missing thermodynamic constants of celsian were calculated in accordance with the methods described in [22, 23]. The equation for the variation of the Gibbs free energy with temperature in the specified reaction has the following form:

$$\Delta G_T = 3111.37 \times 10^3 - 17.07T,$$

where ΔG_T is the free Gibbs energy at temperature T, J/mole.

Thermodynamic analysis of the specified equations shows that sanbornite in the specified range reacts with mullite, whereas celsian and silica coexist. For experimental verification of the results of thermodynamic calculations, mixtures containing celsian and silica in the ratio of 1 : 1 were sintered at temperatures of 1200, 1300, and 1400°C with an isothermic exposure at each prescribed temperature for 6 h. X-ray phase analysis corroborated the presence of

TABLE 1

No.	Elementary triangle	Surface area, ‰
1	$BaO - Ba_8Al_2O_{11} - Ba_3SiO_5$	0.0135
2	$Ba_8Al_2O_{11} - Ba_3SiO_5 - Ba_4Al_2O_7$	0.0125
3	$Ba_3SiO_5 - Ba_4Al_2O_7 - Ba_2SiO_4$	0.0095
4	$Ba_4Al_2O_7 - Ba_2SiO_4 - Ba_3Al_2O_6$	0.0075
5	$Ba_3Al_2O_6 - Ba_2SiO_4 - BaAl_2O_4$	0.0135
6	$BaAl_2O_4 - Ba_2SiO_4 - Ba_3Al_6Si_2O_{16}$	0.0475
7	$Ba_3Al_6Si_2O_{16} - Ba_2SiO_4 - BaAl_2SiO_6$	0.0045
8	$BaAl_2SiO_6 - Ba_2SiO_4 - BaAl_2Si_2O_8$	0.0455
9	$Ba_2SiO_4 - BaAl_2Si_2O_8 - BaSiO_3$	0.0355
10	$BaSiO_3 - BaAl2Si_2O_8 - Ba_2Si_3O_8$	0.0265
11	$Ba_2Si_3O_8 - BaAl_2Si_2O_8 - Ba_5Si_8O_{21}$	0.0055
12	$Ba_5Si8O_{21} - BaAl_2Si_2O_8 - Ba_3Si_5O_{13}$	0.0045
13	$Ba_3Si_5O_{13} - BaAl_2Si_2O_8 - BaSi_2O_5$	0.0450
14	$BaSi_2O_5 - BaAl_2Si_2O_8 - SiO_2$	0.1545
15	$SiO_2 - BaAl_2Si_2O_8 - Al_6Si_2O_{13}$	0.2955
16	$Al_6Si_2O_{13} - BaAl_2Si_2O_8 - Al_2O_3$	0.1175
17	$Al_2O_3 - BaAl_2Si_2O_8 - BaAl_{12}O_{19}$	0.0665
18	$BaAl_2Si_2O_8 - BaAl_{12}O_{19} - BaAl_2SiO_6$	0.0545
19	$BaAl_2SiO_6 - BaAl_{12}O_{19} - Ba_3Al_6Si_2O_{16}$	0.0245
20	$Ba_3Al_6Si_2O_{16} - BaAl_{12}O_{19} - BaAl_2O_4$	0.0565

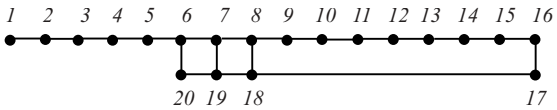

Fig. 2. Topological graph of relationships between the elementary triangles (*1 – 20*) of system $BaO - Al_2O_3 - SiO_2$.

compounds $BaAl_2Si_2O_8$ ($d \times 10^{-10}$ = 7.80, 3.95, 2.96, 2.65, 2.20, 1.85, 1.69, 1.59, 1.52, 1.44 m) and SiO_2 ($d \times 10^{-10}$ = 4.28, 4.07, 2.29, 2.26, 1.85, 1.69, 1.59, 1.57, 1.44 m).

Thus, the data of thermodynamic analysis and the obtained experimental data agree well with the results reported in [5 – 7].

Triangulation of the $BaO - Ba_2SiO_4 - BaAl_2O_4$ zone was carried out using the data obtained in [24]. Using the geometrical analysis method widely used in studying multicomponent systems and that makes it possible to split the systems and their sectors based on the geometrical structure of the diagram without experimental data [25], the following conodes were constructed: $Ba_2SiO_4 - BaAl_2Si_2O_8$, $BaAl_2Si_2O_8 - BaAl_{12}O_{19}$, $Ba_5Si_8O_{21} - BaAl_2Si_2O_8$, $Ba_3Si_5O_{13} - BaAl_2Si_2O_8$.

A complete triangulation of the $BaO - Al_2O_3 - SiO_2$ system was performed based on generalized results of previous studies and studies carried out by us (Fig. 1).

It can be seen that the $BaO - Al_2O_3 - SiO_2$ system is split into 20 elementary triangles and obeys the Kurnakov rule [8]. The surface areas of elementary triangles computed in accordance with the method in [26] are listed in Table 1. The largest surface area belongs to the triangle $SiO_2 - BaAl_2Si_2O_8 - Al_6Si_2O_{13}$ (0.2955‰) and the smallest area is observed in the triangles $Ba_5Si_8O_{21} - BaAl_2Si_2O_8 - Ba_3Si_5O_{13}$ and $Ba_3Al_6Si_2O_{16} - Ba_2SiO_4 - BaAl_2SiO_6$ (0.0045‰).

Figure 2 shows the topological graph of relationships between the elementary triangles in the $BaO - Al_2O_3 - SiO_2$ system. According to the calculation performed, the graph adheres to the Eiler formula [26]. We identified the presence of a suspended point (the graph vertex of power 1), i.e., triangle *1* and also the presence of five inserted triangles (graph apex of power 3), in which neither of the faces is adjacent to the concentration triangle sides: triangles *6 – 8*, *18*, and *19*.

The results of the geometrical-topological analysis of phases are shown in Table 2 and contain data on a number of phases coexisting with a particular phase, the number of elementary triangles in which the particular phase is present, their total relative surface area, and the probability of this phase existing within the concentration triangle [26]. The highest probability of existence in the system relates to the phase $BaAl_2Si_2O_8$ (0.2732‰) that coexists with the greatest number of phases (11), and, consequently, has a substantial stability interval in the system. The least probable is the existence of the phase $Ba_5Si_8O_{21}$ (0.0033‰), which forms part of the triangles with the smallest surface area.

Based on the theoretical and experimental studies performed and generalization of the literary data, the structure of the three-component system $BaO - Al_2O_3 - SiO_2$ in the subsolidus at temperatures of 1200 – 1400°C was refined, the system was completely split into elementary polytypes, and geometrical-topological characteristics of phases comprising the system were supplied. The diagram of subsolidus phase equilibria of the system $BaO - Al_2O_3 - SiO_2$ makes it possible to identify ranges of materials for various destinations in this diagram.

TABLE 2

Compound	Number of triangles in which it is present	Number of phases with which it coexists	Surface area of presence, $S_i \times 1000$	Probability of existence, ‰
BaO	1	2	13.5	0.0045
Al_2O_3	2	3	184.0	0.0613
SiO_2	2	3	450.0	0.1501
$BaAl_{12}O_{19}$	4	5	202.0	0.0673
$BaAl_2O_4$	3	4	108.5	0.0362
$Ba_3Al_2O_6$	2	3	12.0	0.0040
$Ba_4Al_2O_7$	3	4	29.5	0.0098
$Ba_8Al_2O_{11}$	2	3	26.0	0.0087
$BaSi_2O_5$	2	3	168.0	0.0560
$Ba_3Si_5O_{13}$	2	3	119.0	0.0063
$Ba_5Si_8O_{21}$	2	3	10.0	0.0033
$Ba_2Si_3O_8$	2	3	31.0	0.0103
$BaSiO_3$	2	3	62.0	0.0207
Ba_2SiO_4	7	8	154.5	0.0515
Ba_3SiO_5	3	4	35.5	0.0118
$Al_6Si_2O_{13}$	2	3	413.0	0.1377
$BaAl_2Si_2O_8$	11	11	819.5	0.2732
$BaAl_2SiO_6$	4	4	129.0	0.0430
$Ba_3Al_6Si_2O_{16}$	4	4	133.0	0.0443

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